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COMPLEX FORMATION IN METAL DISSOLUTION AND METAL TREATMENT.(U)

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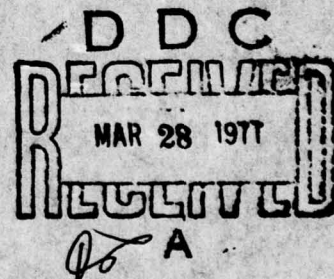
Complex Formation in Metal Dissolution and Metal Treatment

Technical Report No. 6

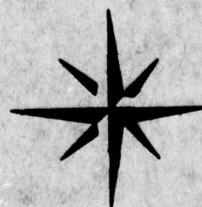
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of iron, stainless steel, and aluminum alloys in halide solutions, the spectrophotometric observation of iron-anion complexes during the dissolution of iron in acid solutions and the decay of the scrape potential in various electrolytic solutions.

New supporting data are presented using relaxation theory treatment of scrape potential and scrape current measurements. Reactions at the interface between oxide-free metal and aqueous solutions take place during time durations similar to those reported for the formation of complexes in solution, also, studied with relaxation techniques. ←

This paper was prepared for presentation at a Symposium on Interfacial Phenomena in Corrosion Protection sponsored by the Division of Organic Coatings and Plastics Chemistry of the American Chemical Society held in New Orleans, March 21, 1977.

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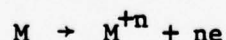
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In the study of metal surface reactions several concepts or approaches have dominated the thinking in the field. These include the electrochemical nature of corrosion, leading to the need to identify anodic and cathodic reactions and their rates; the role of adsorption at the metal-solution interface, and the emphasis on the state of the metal in the crystallographic or topographical sense insofar as it affects the supply of reaction sites. The methods of investigation have followed those proven to be successful in classical chemical kinetics. This involves the construction of a mechanism and the identification of the slow, or rate determining, step. This has justified a tremendous number of studies in the corrosion field centered on hydrogen ion reduction kinetics or oxygen reduction kinetics, appropriately, because in many corrosion reactions these are the slow rate-controlling reactions.

A reconsidering of the nature of metal surface reactions, however, might lead to an alternate and perhaps a more fundamental approach. First, whereas we are concerned with the overall reaction rate as dictated by the slow, or rate determining step, of most significance is the rate of metal dissolution, that is, the manner and rate in which the metal passes from the atomic to the ionic state.

This is the step, this is the reaction, that we eventually must control. Secondly, whereas we define the corrosion process in terms of a metal-environment interaction, extremely little attention has been devoted to the influence of the environment, specifically, the composition of the electrolyte in contact with the metal. Indeed, reaction mechanisms are proposed for metals corroding in concentrated acids that are based on the assumption that the only ions involved are the H^+ and OH^- species.

This reconsideration of surface reaction mechanisms leads to the conclusion that the environment, or the composition of the electrolyte, does play an extremely important part in the corrosion process, further, that this part involves the furnishing of anion species to form complex ions, and finally, that the nature of the complex dictates the ensuing corrosion rate. So, this approach differs in a basic way from the standpoint of where the emphasis should be placed. It is acknowledged that the structure of the metal, along with surface heterogeneities, mechanical stresses, and other physical factors are important. But, the emphasis is now transferred to the solution side of the interface and the environment in which the metal in its ionic form finds itself. In its simplest form, we write the anodic dissolution reaction as



Yet we know that these ionic species never exist, as such, for any length of time in aqueous solutions. Such ions must be hydrated, at least, or immediately form complexes or ion pairs with the anions present in solution. The latter two reactions are favored in concentrated solutions. It has been well demonstrated by several investigators

(1 - 4) that, at the corrosion site of interest, such as in a crevice or in the advancing crack of a stress-corrosion specimen, the solution is indeed concentrated over that of the bulk solution.

This paper, then, examines the concept of the complex ion theory of corrosion (5). The experimental problem becomes one of identifying metal-anion complexes formed at various stages of the metal dissolution reaction and, from their relative stabilities, constructing the mechanism of reaction to include these reaction product species.

EXPERIMENTAL

Recently, three different techniques have been used in our Laboratory to establish the existence of metal complexes as the products of metal dissolution and to attempt to identify these complexes. These techniques were based on establishing the anion-dependence of an electrochemical or physical property related to the corrosion process.

Pitting Initiation Studies

An electrochemical technique was devised by Engell and Stolica (6), and later used by Hoar and Jacob (7), to measure the kinetics of the breakdown of passivity in iron and stainless steels. The technique has been applied to the study of pitting in aluminum alloys by Bogar and Foley (8), Foroulis and Thubrikar (9), and, more recently, by Dallek and Foley (10). In this technique, the metal electrode is held potentiostatically in the passive range in an appropriate

electrolyte; a specific concentration of a salt containing the anion under investigation is injected into the reaction cell; and the induction time, τ , for a sharp rise in current is recorded. It is possible to derive a rate equation (8) as

$$\frac{1}{\tau} = k[M]^m [X^-]^n$$

where k is the rate constant, $[M]$ is the metal ion concentration, $[X^-]$ is the concentration of the anion under investigation, and n and m are the respective orders of reaction. The activity coefficients are included in k . The logarithmic form of the rate equation is

$$\log \left(\frac{1}{\tau} \right) = \log k + m \log [M] + n \log [X^-]$$

If $\log k$ and $m \log [M]$ are taken as constant, then a plot of the logarithm of the reciprocal of the induction time against the logarithm of the anion concentration will give n . This is the number of anions involved in the primary pitting reaction. The term, $m \log [M]$, is probably only constant for a specific metal-anion reaction. The reaction order, m , is considered to be the number of metal atoms involved in a surface site, analogous to the concept of giving the metal surface a coordination number as has been done by Laidler and others (11) in the development of the theory of absolute reaction rates for surfaces.

This particular technique then allows the determination of the stoichiometry of the interfacial reaction or, " n ", the number of anions associated with one metal atom (or metal cation) during the primary pitting process. Also, from experiments conducted at different

temperatures, it is possible to calculate an apparent activation energy for the process and, from its magnitude, attempt to correlate the pitting mechanism with chemical or physical rate determining processes.

Spectrophotometric Observation of Complexes

In this experiment the metal cylinder (iron) is allowed to dissolve in an electrolyte in a spectrophotometer cell of 100 mm path length. The long path length increases the sensitivity of the detection method. An Hitachi EPS-3T spectrophotometer, with an optical cell with far uv silica windows, was used to measure the absorption of the solution in the uv and visible range (12). With this technique it is possible to identify reaction product species that are produced, as a function of time, in acid solutions containing different anions. A serious limitation with the spectrophotometric method as used here is the time required to make a measurement. Thus it is possible to measure the production of species in time intervals of seconds and minutes but not milliseconds.

Scrape Potential Measurements

In the scrape potential measurement (13), a rod of the metal under study, in this case an aluminum alloy, is rotated at high speed in the solution of interest. An agate cutting edge is brought up to the surface and the metal surface is scraped free of the oxide layer and double layer. For an active metal the potential goes rapidly in the negative direction and the most negative value reached is identified as V_{sc} , the scrape potential. This potential decays in the positive

direction, at first very rapidly and then more slowly until a steady state potential, V_{ss} , is reached. At this point the oxide film has been substantially rebuilt. The rate at which the potential decays is measured and actually two rates are observed. The first rate is quite rapid. This rate is labeled dV/dt_1 , and refers to the time range from 0 to 0.25 sec. This is interpreted as a measure of the rate of initial formation of the reaction product film. It had been shown by Hagyard and Williams (14) that the $Al \rightleftharpoons Al^{+3} + 3e$ couple was established in the microsecond range, so what is being measured by dV/dt_1 is the effect of the reaction of Al^{+3} ions with anion species in the electrolyte. The second decay rate, dV/dt_2 , refers to the time interval between 0.25 and 12 seconds. This must measure the rate of growth of the reaction product film toward the steady state structure and composition. Thus, a scrape potential measurement yields the following five parameters:

V_{sc} = the scrape potential

V_{ss} = the final steady state potential

$\Delta V = V_{sc} - V_{ss}$

$\frac{dV}{dt_1}$ = the initial very rapid decay rate

$\frac{dV}{dt_2}$ = the later, slower, decay rate

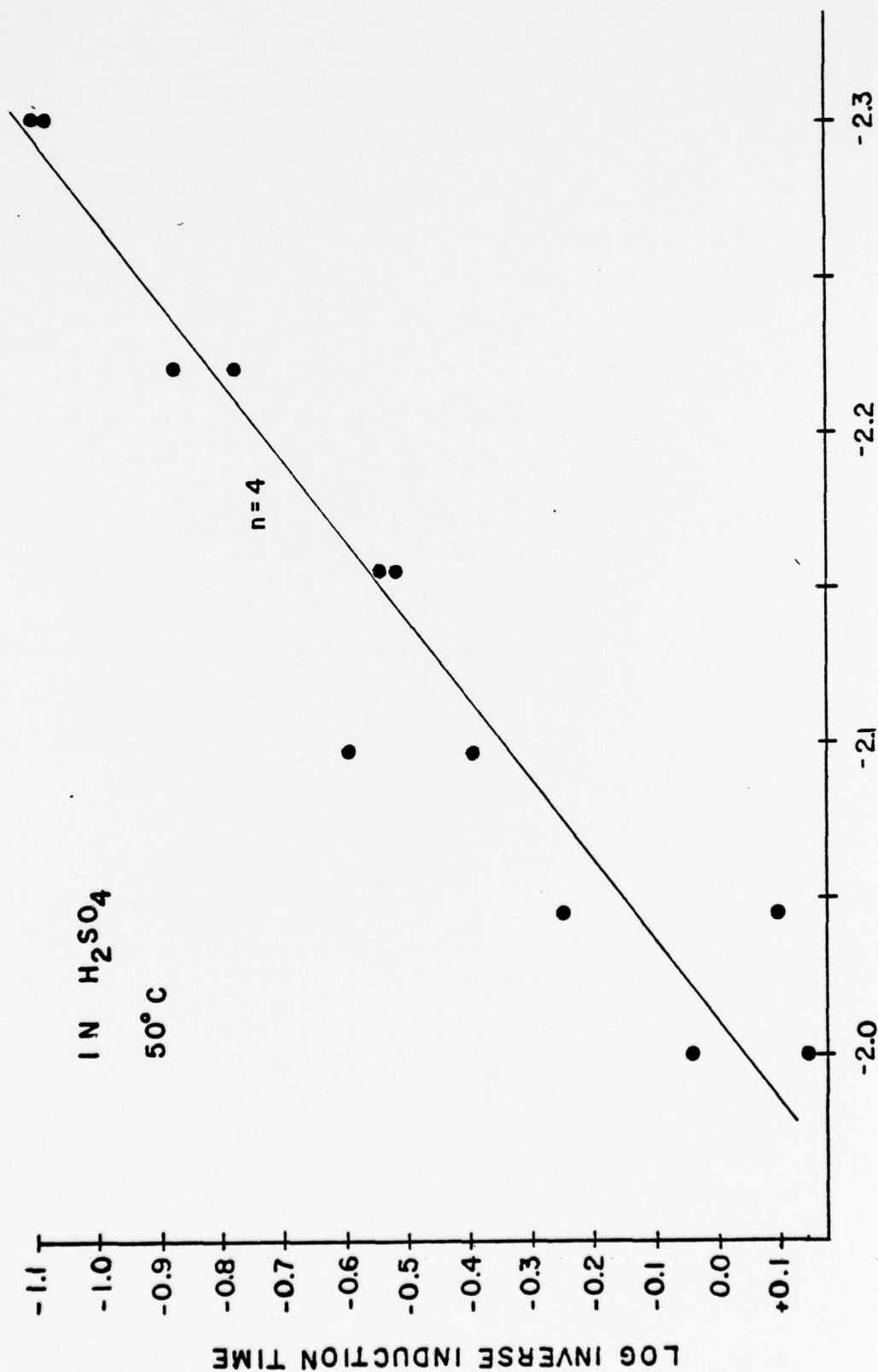
Recently (15), the scrape potential data have been treated with relaxation kinetics from the viewpoint of considering the scraping procedure a perturbation from the equilibrium state (the passive oxide coated surface).

RESULTS AND DISCUSSION

Pitting Initiation Studies

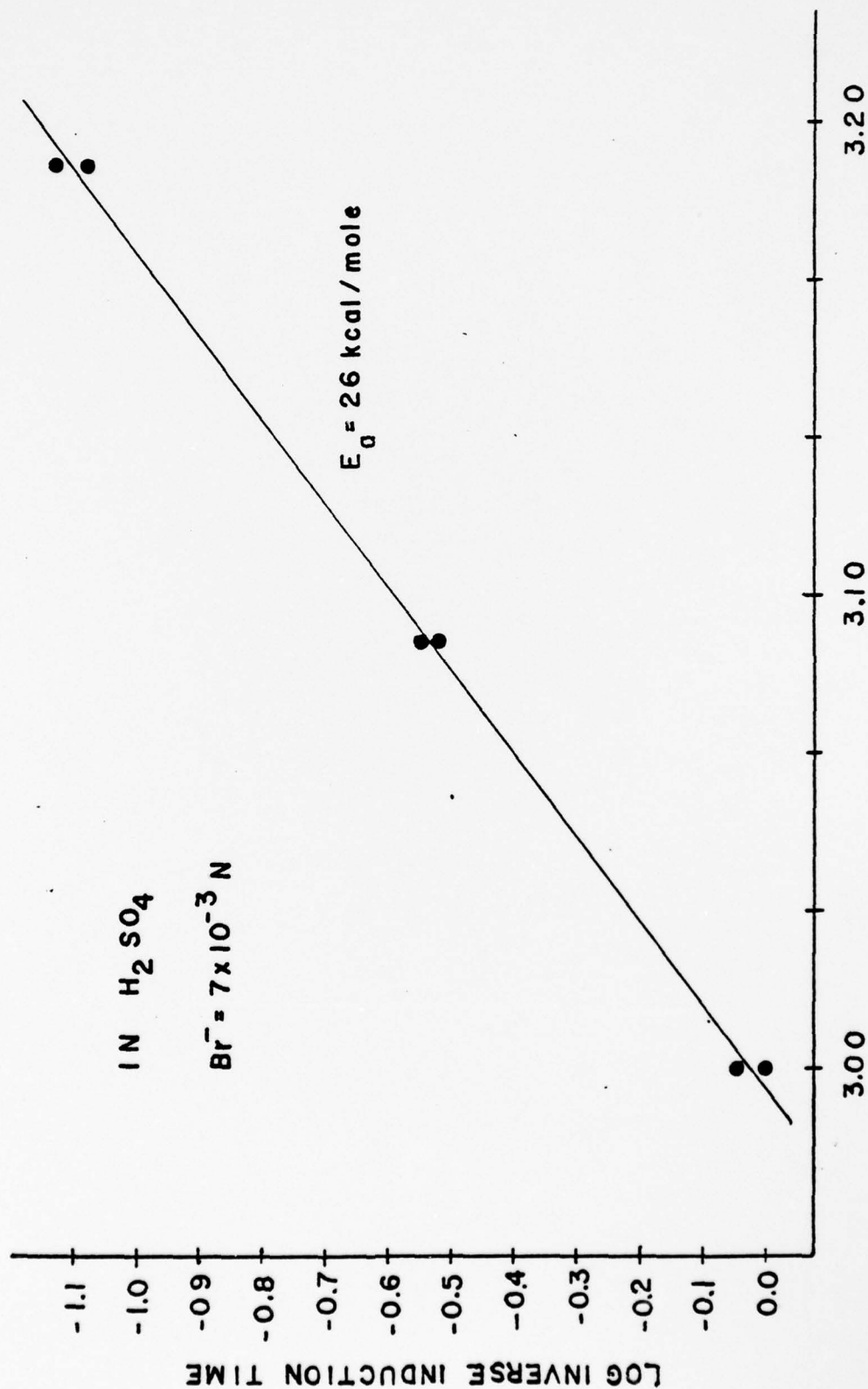
The pitting initiation studies allow a stoichiometric number to be associated with the pitting reaction. The n value is abstracted from a plot similar to that of Figure 1. In that experiment, Al alloy type 7075 was pitted with Br^- ion in 1 N H_2SO_4 at 50°C . Figure 2 gives an Arrhenius-type plot by which the apparent activation energy was estimated. This technique has been used by several investigators to study the pitting of Fe, stainless steel, and four aluminum alloys by halide ions. These results are collected in Table I. Two general observations may be made. The first is that the stoichiometry corresponds to complex formation in solution, i.e., species of the type, AlBr_4^- , are formed. This suggests that our knowledge of complex ion chemistry might be applied directly to these surface reactions. The second observation refers to the relatively high activation energy. In acid solution this usually runs to 20.0 kcal. The value for the pitting reaction on stainless steel was about 60 kcal (7). This definitely suggests a chemical reaction as opposed to certain physical reactions. For example, it would be expected that an adsorption process or a diffusion process would yield a lower activation energy, e.g., that observed with I^- on Al alloy type 7075.

At neutral pH's the reaction order with respect to halide ions for aluminum alloys is usually 1 or 2. This is interpreted to mean the formation of such species as $\text{Al}(\text{OH})_2(\text{Cl})_2^-$. The stoichiometric number for the fluoride reaction is 3 and insoluble AlF_3 is formed on



LOG BROMIDE ION CONCENTRATION

Figure 1 Dependence of the Induction Time for Pit Initiation on $[\text{Br}^-]$ in 1 N H_2SO_4 (pH=0.3) at 50°C.



INVERSE TEMPERATURE $\times 1000$

Figure 2. Arrhenius-type Plot for Temperature Dependence of Induction Time
 in 1 N H_2SO_4 (pH=0.3). $[Br^-] = 7 \times 10^{-3} N$

Table I. Stoichiometric number associated with pitting initiation reaction on metals.

Metal	Anion	pH	"n" Number of Anions per Metal Atom	ΔE Energy of Activation kcal	References
Fe	Cl ⁻	1NH ₂ SO ₄	3	-	(6)
18 Cr, 8Ni-Fe	Cl ⁻	2	2.5-4.5	60	(7)
	Br ⁻	2	4.0-4.5		(7)
Al(1199)	Cl ⁻	0.00	4.0	22.9	(8)
	Cl ⁻	3.50		20.7	(8)
	Cl ⁻	6.08		12.0	(8)
Al(2024)	Cl ⁻	0.0	3.0	-	(8)
	Cl ⁻	3.50	4.8	-	(8)
Al(7075)	F ⁻	5.8	3	4.6	(10)
	Cl ⁻	0.3	8	18	(10)
		5.8	2	12	(10)
	Br ⁻	0.3	4	26	(10)
		5.8	2	10	(10)
	I ⁻	0.3	2	6.6	(10)
Al(99.99%)	Cl ⁻	5.9-6.1	1		(9)

the electrode surface.

Spectrophotometric Observation of Complexes

Iron was allowed to corrode in acid solutions at constant pH of NaCl, NaBr, NaI, NaNO₃, Na₂HPO₄, Na₂SO₄ and NaClO₄ (12). The reactions were carried out under three conditions: a) in an air saturated solution, b) in solutions purged with N₂, and c) in a closed argon-purged system, which should be considered oxygen-free. The spectra were recorded over the uv and visible range as a function of time. While there were many common features in the spectra observed, for each solution the spectrum was unique, i.e., the reaction product species at constant pH were anion dependent.

It is generally considered that the perchlorate ion does not form complexes with ferrous or ferric ions. The observed absorption peak at 230 nm (Figure 3) was associated with the species, $\text{Fe}(\text{H}_2\text{O})_6^{++}$. The spectra obtained from iron corroding in H₂SO₄, Na₂SO₄, NaCl, FeCl₂ and FeCl₃ all contained an absorption peak close to 300 nm but in all the chloride solutions this peak initially increased and then subsequently decreased in intensity. The absorption curves obtained in the chloride solutions (Figure 4) were interpreted in terms of the formation of an unstable ferrous chloride complex followed by hydrolysis to form a more stable species. The spectra obtained in solutions of NaNO₃ in the N₂ purged system (trace O₂) and the closed argon system (O₂ free) were quite similar and were most distinctive when compared to that produced by other anions. Figure 5 reports the spectra obtained with Fe corroding in 0.05 M NaNO₃ at a pH of 1.35. None of the peaks observed in the

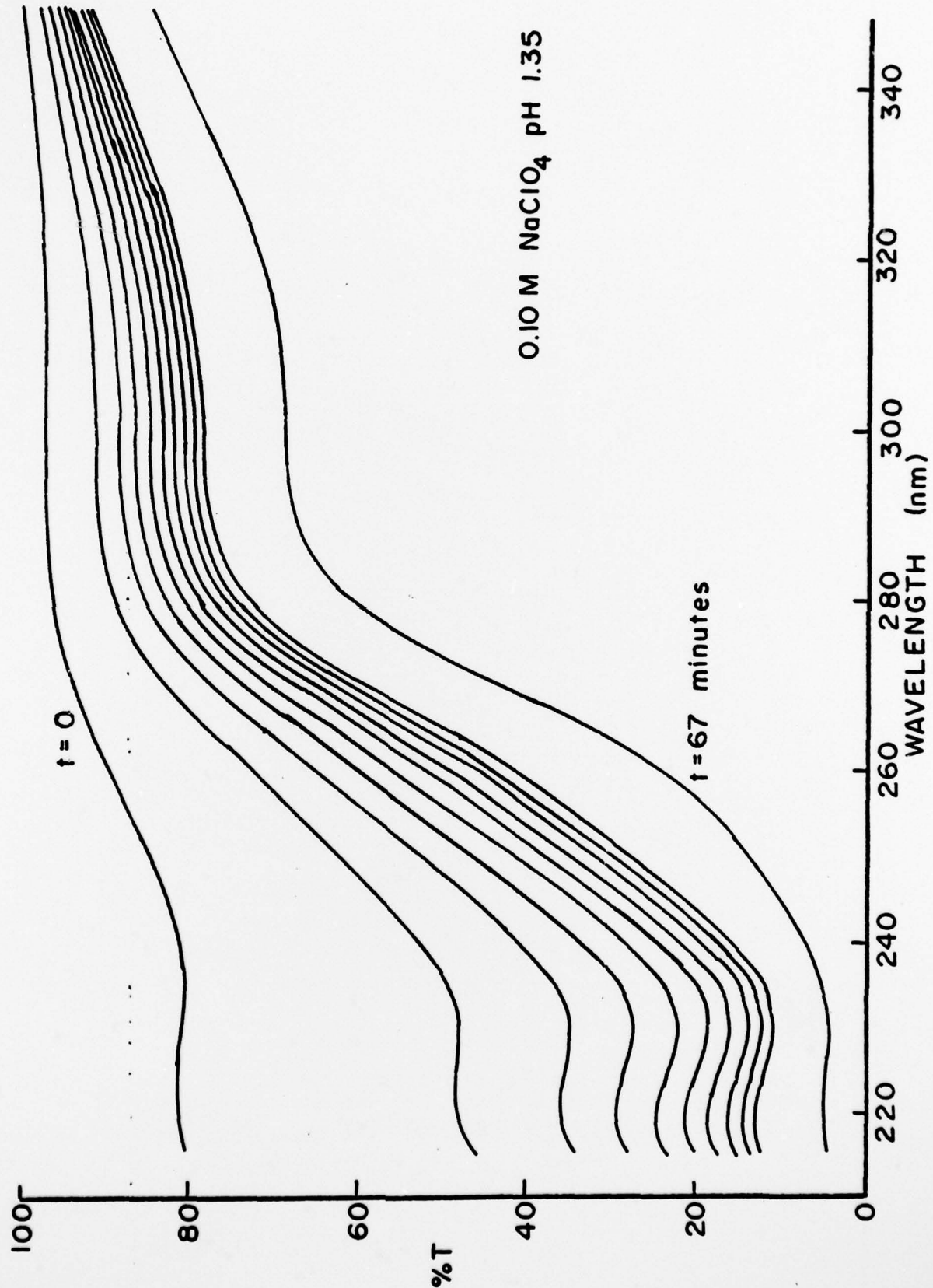


Figure 3. UV spectra of corroding iron in 0.10 M NaClO_4 at pH 1.35

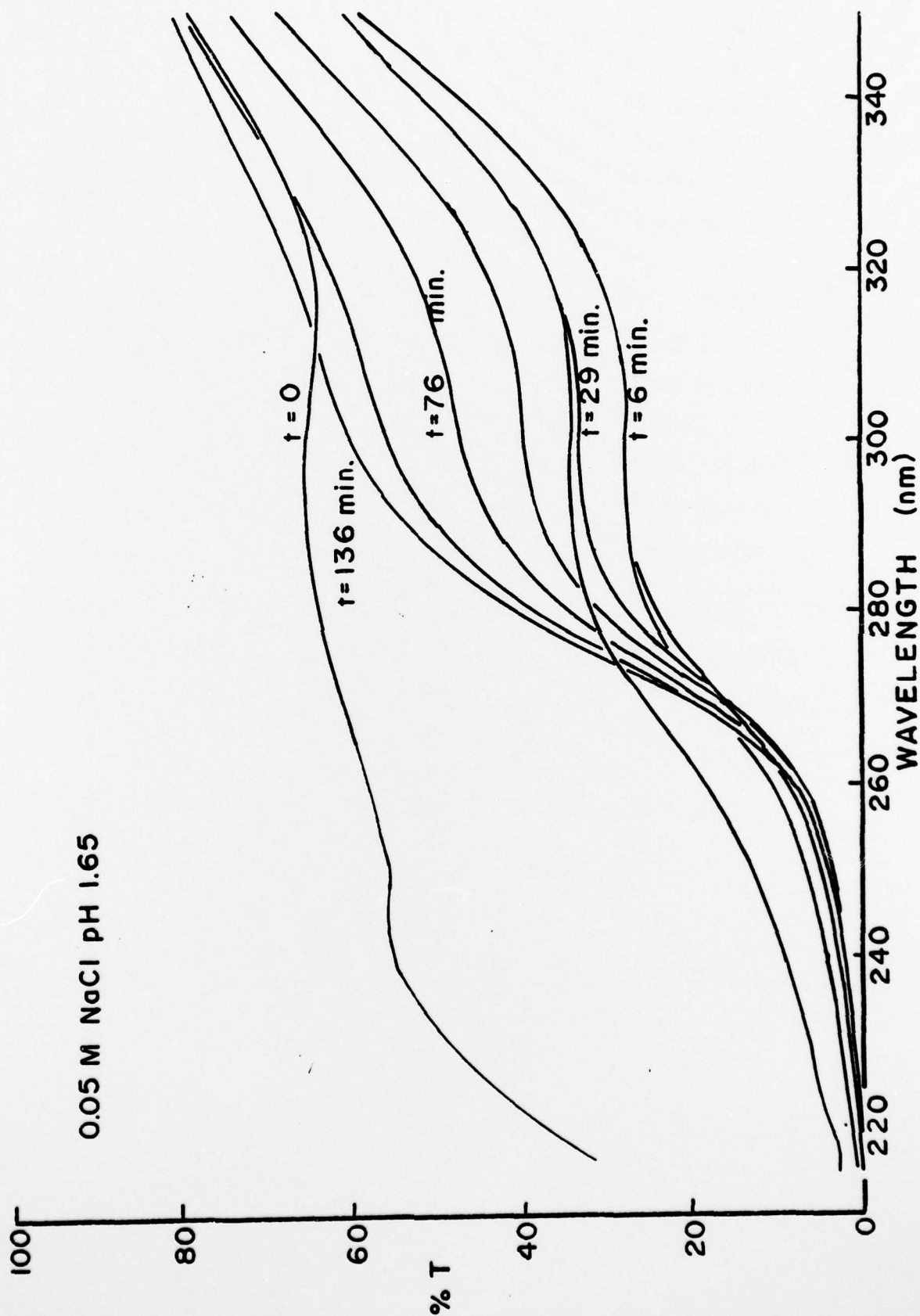


Figure 4 UV spectra of corroding iron in 0.05 M NaCl at pH 1.65

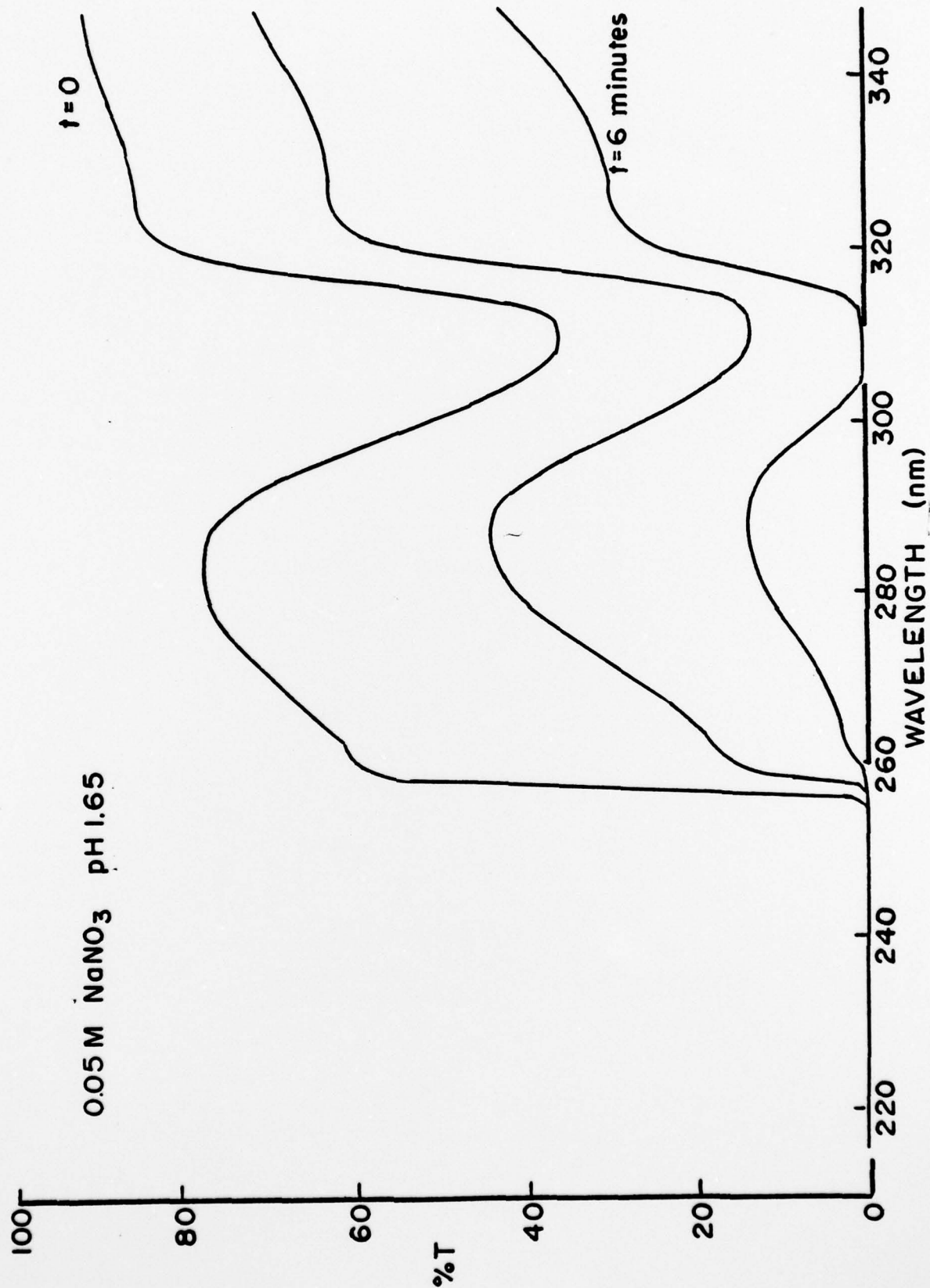


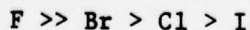
Figure 5 UV spectra of corroding iron in 0.05 M NaNO_3 at pH 1.65

spectrum of the corroding iron-nitrate system could be attributed to absorption by $\text{Fe}(\text{NO}_3)_3$ or other ferric species. It was concluded that certain peaks in the visible spectrum for iron corroding in nitrate solutions were due to ferrous nitrate and ferrous nitrosyl species.

It may be generalized from these studies that the reaction product species formed by iron dissolving in acid solution is anion dependent. Further these species are transitory, appearing and then disappearing as the process continues. These transitory complexes, with the exception of the iron-nitrate complex hydrolyze with time and form the stable $\text{Fe}(\text{H}_2\text{O})_6^{++}$ species.

Scrape Potential Measurements

The scrape potential has been shown to be a mixed potential established by the relative rates of the anodic and cathodic reactions (13). At constant pH and water activity, this potential is controlled by the anodic potential which, in turn, is controlled by the aluminum ion activity. The aluminum ion activity, in turn, is established by the extent to which the ion is tied up as a complex or compound. It is evident from the values of the observed scrape potentials (Figure 6) that they are anion dependent in less concentrated solutions, i.e., up to 1.0 M. Thus at a concentration of 0.5 M the scrape potentials vary in the order:



At the higher concentration the anion dependency is less significant.

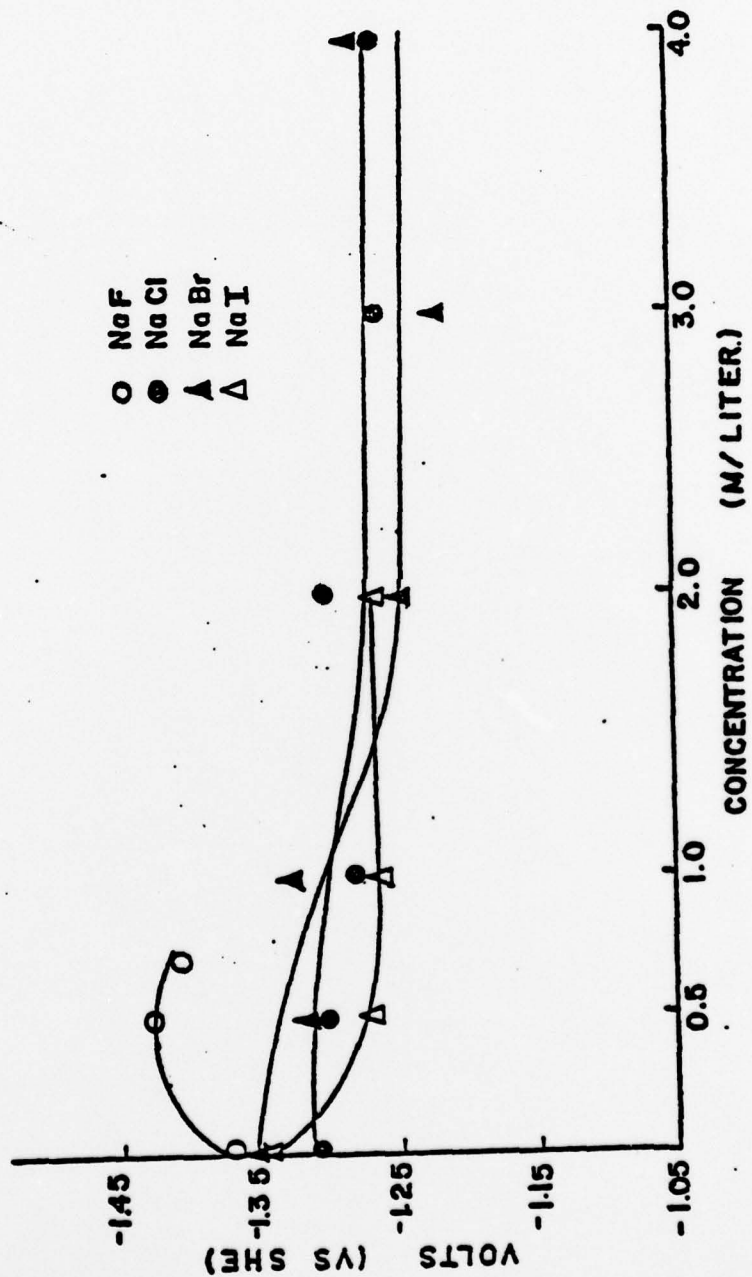


Figure 6 A graph of V_{sc1} vs. concentration for Aluminum Alloy Type 7075-T6 in halide solutions.

Two rates of decay of potential are recorded, of which the first, dV/dt_1 , is more anion dependent, as observed in Table II. The final reaction product film, the hydrated oxide, must be formed by a series of reactions, the first of which is the ionization of the atomic aluminum to the aluminum ion in a microsecond range. Assuming a rapid reaction of the aluminum ion with the anion, then the early reactions must involve the formation of such species as $AlBr_4^-$ which reacts with water to form such species as $Al(OH)_3$ or $Al_2O_3 \cdot H_2O$. Thus the stability of the intermediate species is all important. The so-called aggressive ions will lower the dV/dt_2 , i.e., on a competitive basis resist the formation of the (passive) reaction product film. Ions, such as sulfate and chromate favor the rapid formation of the oxide film.

If we assume that the oxide-coated aluminum rod is in a state of equilibrium, the scraping procedure may be visualized as a perturbation of the system from equilibrium and capable of being treated by relaxation kinetic theory (15). When this is done, specific rates of the formation of the complexes may be calculated. These rates are given in Table III and it is of interest to note that these are similar in magnitude to rates reported for the complexation of ferric ions with halide ions (16) and aluminum ions with sulfate ions (17).

CONCLUSIONS

The concept under investigation predicts that transitory complexes are formed during metal dissolution. It is the relative stability of these complexes that direct the path of further reaction and dictates

Table II. Aluminum Alloy 7075-T6

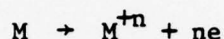
dV/dt₁ , dV/dt₂ Values For Various Anions

Solution	pH	dV/dt ₁ volt sec ⁻¹	dV/dt ₂ volt sec ⁻¹
0.01 N NaF	6.70	1.20	0.09
0.5 N NaF	7.10	0.70	0.03
0.7 N NaF	6.70	0.70	0.05
0.01 N NaCl	5.62	0.40	0.12
0.5 N NaCl	5.80	0.90	0.08
1.0 N NaCl	5.84	0.70	0.08
2.0 N NaCl	5.80	0.70	0.07
3.0 N NaCl	5.80	0.70	0.06
4.0 N NaCl	6.10	0.70	0.08
0.01 N NaCl	1.00	1.1	0.11
0.05 N NaCl	1.05	2.6	0.10
1.0 N NaCl	0.80	2.5	0.08
2.0 N NaCl	0.70	2.5	0.10
0.01 N NaBr	6.2 - 6.62	0.75	0.10
0.5 N NaBr	6.52	1.20	0.07
1.0 N NaBr	6.20	2.40	0.10
2.0 N NaBr	7.45	1.40	0.09
3.0 N NaBr	7.90	1.10	0.07
4.0 N NaBr	6.85	1.10	0.08
0.01 N NaBr	1.10	1.20	0.10
0.5 N NaBr	1.10	2.10	0.11
1.0 N NaBr	1.00	1.70	0.08
4.0 N NaBr	0.80	2.30	0.07
0.01 N NaI	5.50	0.70	0.08
0.5 N NaI	5.7 - 6.3	1.20	0.07
1.0 N NaI	5.9 - 8.1	1.20	0.07
2.0 N NaI	6.2 - 8.3	1.40	0.06
H ₂ SO ₄	1.40	3.2	0.05
NaOH	10.90	0.32	0.05

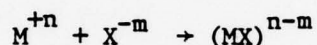
Table III. Specific rates for the formation of aluminum halide complexes at neutral pH.

$\text{Al}^{+++} + \text{X}^- \xrightleftharpoons[k_b]{k_f} \text{AlX}^{++}$				
<u>Solution</u>	<u>pH</u>	k_f <u>sec⁻¹</u>	k_b <u>sec⁻¹</u>	$K = \frac{k_f}{k_b}$
NaF	6.7 - 7.0	0.83	16.6	0.050
NaCl	5.6 - 6.1	17.4	4.3	4.08
NaBr	6.6 - 7.9	22.6	9.7	2.31
NaI	5.5 - 6.3	32.8	7.4	4.41

whether the metal will dissolve rapidly, on one hand, or quickly achieve passivity on the other. Obviously, in some environments, given the proper complexing agents, a metal cannot ever achieve passivity. Thus, the path of metal dissolution must follow the following steps: The first step is rapid



The next step, also rapid, is the formation of the complex



The properties of $(MX)^{n-m}$ dictate the reactive or passive property of the metal in corrosion or surface reactions. Often, this complex reacts



and this reaction makes the observation of these complexes difficult. The existence of the complex is a dynamic one characterized by such reactions as outer-inner sphere reactions, hydrolysis, ion exchanges, or even hydroxide formation.

The experiments cited above offer collaborative evidence for this concept. Previously other lines of evidence had been cited in support.

Among these are the feasibility of assigning specific ions to either the anodic or cathodic part of the corrosion process (18). Sulfate ion is involved in the cathodic process whereas chloride ion is involved in the anodic.

It has been observed that anions have specific effects on inhibitors, e.g., chloride ion interferes with "anodic" inhibitors but not "cathodic" (18).

The electrochemical reaction order for the dissolution of iron in concentrated solutions depends on the chloride ion concentration (19).

The corrosion of iron is inhibited by ferrous chloride in very concentrated acid solutions (20).

The anodic corrosion current for iron in various electrolytes is a function of the anion in solution, perchlorate > sulfate > chloride > acetate > nitrate (21).

The adsorption of chloride and sulfate ion on iron is interdependent, may be competitive or synergistic (22).

The activation energies for the corrosion of iron in acid solution varies with different anions (23). The measurements were at constant pH.

Some of the most widely quoted mechanisms for the dissolution of iron in acid solution assumes the formation of species such as $\text{Fe}(\text{OH})^+$ as intermediates (21,24). No evidence for such species were observed in the spectrophotometric studies reported above. This is not surprising as the anion/hydroxide ratio, for example, is of the order of 10^{13} in these solutions and it is well acknowledged that such adsorption processes are competitive and concentration dependent. It is further unlikely that hydroxyl ions could come from the metal reaction with adsorbed water as the reaction rate of OH^- with H^+ of $1.5 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, reported

by Eigen (25) is much too fast to allow $\text{Fe}(\text{OH})^+$ species to participate in an inner-outer sphere reaction.

In a cumulative sense there is a predominance of evidence supporting this concept of the role of complexes in metallic dissolution processes.

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